

Band alignment at the *i*-ZnO/CdS interface in Cu(In,Ga)(S,Se)₂ thin-film solar cells

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The interface between the *i*-ZnO layer and the CdS buffer in Cu(In,Ga)(S,Se)₂ thin-film solar cells from the Shell Solar baseline process has been investigated using ultraviolet- and x-ray photoelectron spectroscopy and inverse photoemission. Combining both techniques, a direct determination of the conduction and valence band offsets at the interface is possible. Different from existing models, we find a flat conduction band alignment (i.e., a conduction band offset of 0.10 ± 0.15 eV), ~ 0.5 eV above the Fermi level, and a valence band offset of 0.96 ± 0.15 eV.

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Thin film solar cells based on polycrystalline Cu(In,Ga)(S,Se)₂ (CIGSSe) have already reached high efficiencies, both on a laboratory scale [19.2% (Ref. 1)] as well as on large areas (13.4% on 3459 cm²).² They consist of a multilayer structure, in most cases in the following sequence: front contact/CdS/CIGSSe/Mo/glass. The front contact has to fulfill competing requirements. Apart from a high conductivity for minimizing the resistance in the cell, a large band gap is desired for maximum transparency in the relevant photon energy range. For CIGSSe solar cells in most cases a two layer structure consisting of intrinsic ZnO (*i*-ZnO) and *n*-doped ZnO is used. It is understood that the *n*-ZnO layer functions as the transparent and well-conducting front contact. In contrast, the beneficial role of the *i*-ZnO layer is not understood. Rau *et al.*³ propose that the *i*-ZnO reduces the impact of lateral electronic inhomogeneities, caused by absorber crystallites with different electronic properties.⁴ One of the important parameters for an understanding of the *i*-ZnO layer is the band alignment at the interface towards the CdS buffer layer. In particular the conduction band offset is of great interest, because *electrons* need to be transported from the CIGSSe absorber to the front contact.

Ruckh *et al.* have used photoelectron spectroscopy (PES) for a determination of the valence band offset (VBO) with CdS films evaporated onto rf-sputtered polycrystalline ZnO and find a value of 1.2 (± 0.1) eV.⁵ By using reference bulk band gaps they deduced a conduction band offset (CBO) of -0.3 (± 0.1) eV [a negative CBO means that the conduction band minimum (CBM) of CdS lies above that of ZnO]. Similarly, Säuberlich *et al.* have evaporated CdS onto a sputtered *i*-ZnO layer.⁶ Their values for the VBO scatter between 0.82 (± 0.1) and 1.2 (± 0.1) eV, depending on the

conditions during the ZnO preparation. In addition Nguyen *et al.* found that the position of the Fermi level within the *i*-ZnO band gap may also depend on the doping level of the buffer layer.⁷ We thus conclude that it is important to investigate the real sample structure, i.e., samples which are as close as possible to the industrial process used for cell production. Furthermore, our recent experiments have shown that for the CdS/CIGSSe interface a *direct* determination of the conduction band offset using PES and inverse photoemission (IPES), is very important.^{8,9} It is thus the purpose of this letter to report on the band alignment at the real *i*-ZnO/CdS interface (as used in the Shell Solar base line) by combining PES and IPES. As will be shown, we find a flat conduction band alignment and a significant separation of Fermi energy and CBM in the *i*-ZnO film.

All samples were taken directly from the Shell Solar base line process in which the CIGSSe absorber is prepared by rapid thermal annealing of elemental layers on Mo-coated soda-lime glass in a sulfur-containing atmosphere, as described in Ref. 10 and references therein. Then, a CdS layer is deposited by a standard chemical bath deposition. For the present study, *i*-ZnO layers of different thickness were then deposited on the CdS/CIGSSe/Mo/glass structure by magnetron sputtering. For a determination of the band offsets and an investigation of the interface formation, two thin layers (nominal thickness 3 and 5 nm) and a thick layer of 25 nm were used.

All samples were investigated with ultraviolet PES (UPS) using He I and II excitation, x-ray PES (XPS) with a Mg K_α source, and IPES. The PES spectra were measured with a VG CLAM 4 analyzer. For the IPES experiments, a Cicacci-type electron gun and a Dose-type detector with SrF₂ window and Ar:I₂ filling were used. All experiments were performed in ultrahigh vacuum with a base pressure

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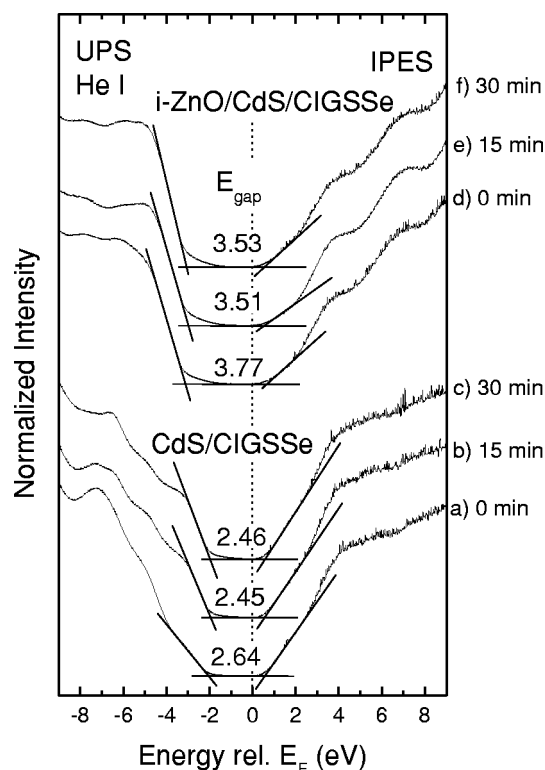


FIG. 1. He I UPS (left) and IPES (right) spectra of CdS/CIGSSe (a)–(c) and ~ 20 nm *i*-ZnO/CdS/CIGSSe (d)–(f) after subsequent Ar^+ sputter steps (50 nA/cm^2 , 50 eV, sputter times are given at the right ordinate). The VBM and CBM were determined by linear extrapolation of the leading edges. The resulting surface band gaps are given for each pair of spectra.

below 5×10^{-10} mbar. Throughout the experiments, great care was taken to detect potential charging effects, but, even for the thickest *i*-ZnO film, no such effects could be found.

The XPS measurements show a surface contamination with C and O on all samples as they naturally occur during a low-cost production process by air exposure. In order to reduce the surface species, all samples were carefully cleaned by mild Ar^+ ion sputtering. To minimize sputter damage, we have used very low ion energies (50 eV) and low currents ($\sim 50 \text{ nA}/\text{cm}^2$) at low incidence angles. It is well known that prolonged sputtering of CIGSSe with 500 eV Ar^+ leads to the formation of metallic In and Cu,^{9,11} but we did not find any evidence for such effects on CIGSSe, CdS, or ZnO when using an ion energy of 50 eV. O and C contaminations, in contrast, are removed very well by this treatment, as seen in the XPS measurements (not shown here). For the untreated samples, the valence and conduction band spectra are dominated by the contamination layer (as seen in spectra *a* and *d* of Fig. 1) which leads to a seemingly increased band gap for the contaminated CdS and ZnO surfaces. To determine the band gap, the valence band maximum (VBM) and the conduction band minimum (CBM) are derived by a linear extrapolation of the leading edge in the spectrum (for a justification of this procedure see Ref. 12). After two 15 min sputter treatments the surface contaminations are completely removed and the valence and conduction bands of CdS and ZnO show their representative spectral signature (see spectra *b*–*c* and *e*–*f* in Fig. 1). Having thus obtained relevant values for the VBM and the CBM of both materials we can derive the surface band gap values, which are $2.46 (\pm 0.15)$ eV for

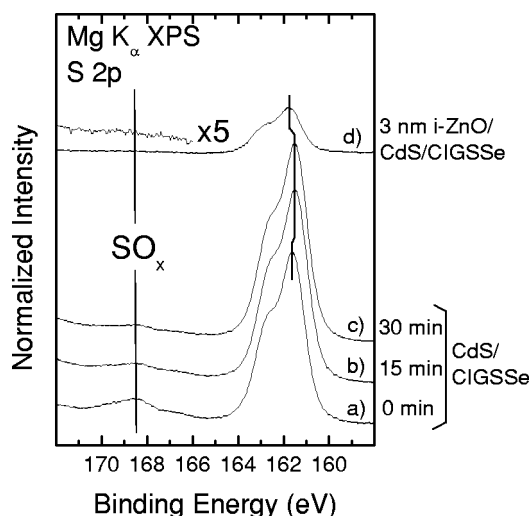


FIG. 2. $\text{S } 2p$ XPS spectra of the CdS/CIGSSe surface before (a) and after Ar^+ sputter treatment (50 nA/cm^2 , 50 eV, sputter times are given at the right ordinate) (b) and (c), indicating oxidized sulfur at the surface. The spectrum of a 3 nm thin *i*-ZnO layer on top of the CdS/CIGSSe structure (d) shows the removal of SO_x by the *i*-ZnO magnetron sputtering process.

the CdS surface and $3.52 (\pm 0.15)$ eV for the *i*-ZnO surface. The latter is slightly larger than the generally accepted bulk band gap [3.35 eV (Ref. 13)]. This discrepancy is attributed to a fundamental problem of determining the correct (*k* resolved) VBM with UV photoemission due to a potential lack of suitable photoemission final states at the Γ point (see, e.g., Ref. 12 and references therein). In the present case, we note a significant pre-edge intensity in the ZnO valence band spectrum, which presumably contains the “true” VBM as well as defect induced emission. The determination of the conduction and valence band offsets is done in two steps. In the first step the CBM (VBM) values of the CdS surface are compared with those of the *i*-ZnO surface. In a second step we consider changes of the band bending in the substrate (CdS/CIGSSe/Mo/glass) due to the interface formation process as well as band bending towards the *i*-ZnO surface (together henceforth called interface-induced band bending). This requires at least one additional sample with a very thin *i*-ZnO film on the CdS layer. Comparing the core level line positions of the CdS surface, the thin *i*-ZnO overlayer, and the thick *i*-ZnO film surface, we can compute the corrections for the interface-induced band bending. To increase the data reliability, we measured two thin *i*-ZnO overlayers with a nominal thickness of 3 and 5 nm, respectively.

A closer look at the thin samples also reveals that the CdS surface is modified during the *i*-ZnO sputter deposition process. On the pristine CdS surface we find an oxidized sulfur species (SO_x with $x > 2$, most likely SO_4), as shown in Fig. 2(a). The oxidation is reduced after Ar^+ sputter cleaning [Figs. 2(b) and 2(c)] and also after the sputter deposition of 3 nm *i*-ZnO [Fig. 2(d)]. The *i*-ZnO sputter deposition process apparently removes surface adsorbates as well. Note that there is no trace of oxidized sulfur in the enlarged part of spectrum *d*, while the sulfur main line at 161.5 eV is quite strong, which rules out any attenuation effects. In Fig. 2 also a shift of the main S line can be observed. The shift between Figs. 2(a) and 2(b) is attributed to changes in band bending due to the removal of the surface contaminations by the sput-

ter treatment since no peak broadening is observed. The shift in Fig. 2(d) is due to the interface-induced band bending occurring after the *i*-ZnO deposition, which will be quantified below.

By analyzing the positions of the respective conduction band edges, we derive values of $0.52 (\pm 0.10)$ and $0.50 (\pm 0.10)$ eV for the CBM of CdS and *i*-ZnO, respectively. Thus, the first (approximative) step of our analysis determines a vanishing conduction band offset. Also, the results indicate that in both layers a significant separation between the Fermi energy and the CBM exists.

For the second step in determining the band alignment, we have quantified the interface-induced band bending by using different combinations of CdS and *i*-ZnO core level lines (Cd 3*d*, S 2*p*, Zn 2*p*, Zn 3*p*, and O 1*s*). In total, twelve different values were obtained, all of which lie within 0.12 eV. The average value is $0.12 (\pm 0.10)$ eV, which arises from a small downward shift of the electronic levels in CdS due to the interface formation and a small downward shift of the ZnO levels with increasing thickness (band bending). Combining this interface-induced band bending correction with the observed CBM values we derive a CBO of $0.10 (\pm 0.15)$ eV, indicating that the band alignment is essentially flat, with the CBM of the *i*-ZnO slightly above the CBM of the CdS layer. For the VBO we find a value of $-0.96 (\pm 0.15)$ eV.

A complete picture of the band alignment at a real interface should also include possible intermixing processes. In fact, we have used a combination of PES, IPES, and *SL*_{2,3} x-ray emission spectroscopy (XES) to show that the band alignment at the CdS/Cu(In,Ga)Se₂ interface is strongly influenced by an intermixing of S and Se.⁸ In the present case we have checked the attenuation behavior of the Cd 3*d* and S 2*p* lines for different *i*-ZnO thicknesses and performed XES measurements of the *i*-ZnO/CdS interface (not shown), but found no indication for intermixing processes.

The resulting band alignment is summarized in Fig. 3. We find a flat conduction band alignment and a correspondingly large VBO. Furthermore, we find that the used magnetron sputtering process of the *i*-ZnO layer modifies the CdS surface by removing surface oxides on the CdS which form during or after the fabrication process. The measurements presented here show that the common picture of the *i*-ZnO/CdS band alignment, which suggests that the Fermi level is very close to the conduction band minimum of the *i*-ZnO layer,^{3,14,15} is not valid for the materials and fabrication processes applied here. Furthermore, the present results, together with our previous work on the CdS/CIGSSe interface,⁹ indicate a predominantly flat conduction band alignment throughout the complete *i*-ZnO/CdS/CIGSSe sandwich structure. Hence it is of great importance to modify existing models with significant conduction band offsets in

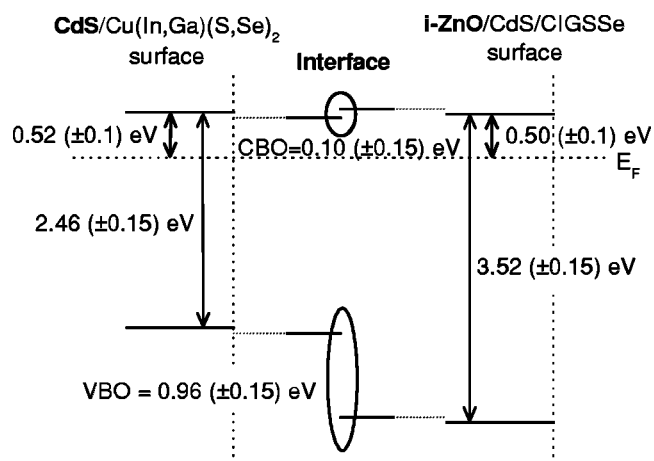


FIG. 3. Schematic diagram of the band alignment at the *i*-ZnO/CdS interface. The VBM and CBM of the CdS and *i*-ZnO films (as determined by UPS and IPES) are shown on the left and right, respectively. The center shows the band alignment at the interface after taking the interface-induced band bending into account.

order to achieve a better understanding of the electronic properties of CIGSSe thin film solar cell devices.

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